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Thermal Stability of Hi-Nicalon SiC Fiber in Nitrogen and Silicon Environments

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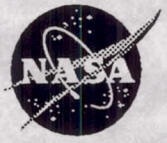

National Aeronautics and
Space Administration

THERMAL STABILITY OF HI-NICALON SIC FIBER IN NITROGEN AND SILICON ENVIRONMENTS

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SUMMARY

The room temperature tensile strength of uncoated and two types of pyrolytic boron nitride coated (PBN and Si-rich PBN) Hi-Nicalon SiC fibers was determined after 1 to 400 hr heat treatments to 1800 °C under N_2 pressures of 0.1, 2, and 4 MPa, and under 0.1 MPa argon and vacuum environments. In addition, strength stability of both the uncoated and coated fibers embedded in silicon powder and exposed to 0.1 MPa N_2 for 24 hrs at temperatures to 1400 °C was investigated. The uncoated and both types of PBN coated fibers exposed to N_2 for 1 hr showed noticeable strength degradation above 1400° and 1600 °C, respectively. The strength degradation appeared independent of nitrogen pressure, time of heat treatment, and surface coatings. TEM microstructural analysis suggests that flaws created due to SiC grain growth are responsible for the strength degradation. In contact with silicon powder, the uncoated and both types of PBN coated fibers degrade rapidly above 1350 °C.

INTRODUCTION

Continuous SiC fibers derived from polymer precursors are being used as reinforcements of ceramic matrix composites (CMC) for high temperature structural applications. These fibers have a higher strain-to-failure than the ceramic matrix, and this together with an appropriately engineered interface, such as pyrolytic carbon (PC) or pyrolytic boron nitride (PBN) have lead to improved mechanical performance of CMC (refs. 1 and 2). The first generation of polymer derived SiC fibers, such as Nicalon and Tyranno fibers, generally contained β-SiC microcrystals connected by SiO_xC_y grain boundaries and free carbon (ref. 3). It has been shown that the strength of these fibers degrades after a short time exposure (<5 hr) above 1200 °C in inert environments (refs. 4 to 6). The degradation is determined to be associated with the void formation due to decomposition of the SiO_xC_y, and exaggerated growth of β-SiC microcrystals in the fibers (refs. 4 to 6). Because of these problems, CMC fabricated using these fibers are also limited to ~1100°C for long term use. To overcome this problem, a second generation of polymer derived SiC fibers, such as Hi-Nicalon and Hi-Nicalon-S fibers, have been developed. These fibers have a higher elastic modulus and creep resistance than Nicalon SiC fibers and contain near-stoichiometric β-SiC microcrystals, amorphous carbon, and a small amount of silicon oxycarbide (<1 wt %) (refs. 7 to 8). Preliminary studies by Takeda et al. (refs. 9 to 10) indicate that Hi-Nicalon SiC fibers retain their as-fabricated strength after 1 hr exposure at temperatures to 1400 °C in argon. The loss in tensile strength above this temperature was attributed to grain growth and void formation due to decomposition of the SiO_xC_y phase. In a recent study, Shimo et al. (ref. 11) have shown that the temperature of onset of decomposition reaction in these fibers can be delayed to a temperature >1500 °C by heat treating them in nitrogen. These studies indicate that Hi-Nicalon SiC fibers are more stable than Nicalon fibers during high temperature fabrication of silicon-based CMC, such as SiC and Si_3N_4, and may also improve the long term reliability of these composites.

The objectives of this study are to determine the upper temperature capability of uncoated Hi-Nicalon SiC fibers, and to evaluate the strength stability of the uncoated and PBN coated Hi-Nicalon SiC fibers under conditions typically used for the fabrication of reaction-bonded Si_3N_4 (RBSN) composites. The PBN and Si-rich PBN coatings were chosen because of their chemical compatibility and stability with SiC fibers and the RBSN matrix.

EXPERIMENTAL

The uncoated Hi-Nicalon SiC fibers for this study were procured from Dow Corning, Midland, Michigan. The chemical composition of the fiber as reported by the vendor is Si (62.4 wt %), C (37.1 wt %), and O_2 (0.5 wt %). As-received Hi-Nicalon fibers were coated with a 0.5 μm thick PBN or Si-rich PBN layer. The coatings were applied by chemical vapor deposition by Advanced Ceramic Corporation, Cleveland, Ohio. For brevity the uncoated, PBN, and Si-rich PBN coated Hi-Nicalon SiC fibers will be henceforth referred to as the uncoated, PBN, and Si-rich coated fibers, respectively.

For heat treatment, ~125 mm long fibers were placed in separate Grafoil envelops and heat treated either in flowing high purity nitrogen for 1 to 400 hr, or in high pressure nitrogen at 2.5 and 4.0 MPa for 1 hr in the temperature range between 1400° and 1800 °C. Heat treatments were conducted in a furnace equipped with carbon elements and lining. Some fiber specimens were also placed in a loosely packed bed of silicon powder in a alumina boat, and heat treated at 1150, 1250, 1350 and 1400 °C for 24 hrs in high purity nitrogen.

Room-temperature tensile strength of fibers were measured in a universal tensile testing machine at a cross-head speed of 1.3 mm/min using standard fiber mounting procedure (ref. 4). Between 10 to 20 fibers were tested for each exposure condition.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used for microstructural characterization. For TEM analysis, fibers ~3 mm in length were sectioned from the as-received and heat treated fiber tows. Individual 3 mm fibers were then separated from the tows and glued onto a copper grid using a fast drying epoxy. After the epoxy hardened, the whole sample was ion-beam thinned to <300 nm. Microstructure of the longitudinal sections of the fibers was examined and analyzed using a Phillips 400T microscope operating at 120 kV.

RESULTS AND DISCUSSION

Exposure Effects on Tensile Strength

The room temperature tensile strength of the uncoated fibers after heat treatment in 0.1 MPa nitrogen for 1, 10, 100, and 400 hrs in the temperature range between 25 and 1800 °C is shown in figure 1. Each data point represents the average tensile strength of 10 to 20 individual tests. The error bar represents two standard deviations. Tensile strengths were calculated based on an average fiber diameter of 14 μm, even though individual fiber diameters in a tow varied from 9 to 16 μm. According to figure 1, the fibers heat treated up to 1400 °C showed a small loss in strength (<10 percent) compared to the as-fabricated fibers. In this temperature regime, both the temperature and time of exposure had a minor influence on the tensile strength. Above 1400 °C, the strength decreased significantly with increasing time of exposure at any given temperature.

Effects of nitrogen over-pressure on the room temperature strength of the uncoated fibers heat treated at temperatures to 1800 °C for 1 hr are shown in figure 2. This figure indicates that nitrogen pressure had no significant influence on the strength of heat treated fibers up to 1400 °C. Above this temperature, the fibers heat treated under nitrogen pressures of 2.5 and 4.0 MPa showed lower strength than those heat treated in 0.1 MPa nitrogen pressure, but no definite correlation between nitrogen pressure and strength degradation was observed.

To determine environmental effects on their strength, the uncoated fibers were also heat treated for 1 hr in 0.1 MPa argon and vacuum from 25 to 1800 °C and the results are shown in figure 3. Included in the figure for comparison purposes are the data for the uncoated fibers heat treated in the same temperature range in 0.1 MPa nitrogen. All three plots showed similar trends, indicating that the argon, vacuum, and nitrogen environments produced about the same strength loss behavior. This suggests that the strength degradation of the uncoated fibers is primarily a function of temperature of heat treatment and time of exposure, and heat treatment environments play a secondary role.

Thermal exposure effects on the room temperature tensile strength of the PBN and Si-rich PBN coated fibers after heat treatment in 0.1, 2.5, and 4.0 MPa nitrogen for 1 hr from 1400 to 1800 °C are shown in figure 4. The room temperature strengths of uncoated fibers heat treated in 0.1 MPa nitrogen in the same temperature range are also shown in the figure for comparison. It is quite obvious from the figure that the room temperature strengths of the as-fabricated and heat treated PBN and Si-rich PBN coated fibers are in general lower than that of the uncoated fibers. In addition, both the uncoated and PBN coated fibers retained their as-fabricated strength after 1 hr heat treatment up to 1600 °C; but above this temperature, they showed strength loss. Other noticeable features of this plot are that nitrogen over- pressure had no significant effect on the strength degradation of the coated fibers (a behavior similar to that of the uncoated fibers under similar heat treatment

conditions), and that the difference between the average strength of the uncoated and PBN coated fibers at any exposure temperature and time remained nearly the same. This suggests that the surface coating of the fiber does not contribute to the strength except by increasing the cross sectional area and possibly, due to poor quality of the coating, or coating process damaging the fiber surface. It should be mentioned that the Si-rich PBN coated fibers showed a slight increase in room temperature strength with increasing temperature of heat treatment up to 1600 °C, but above this temperature these fibers also degraded similar to the uncoated fibers.

Figure 5 shows the room temperature tensile strength of the uncoated, PBN coated, and Si-rich PBN coated fibers after being embedded in silicon powder and heat treated in 0.1 MPa nitrogen at 1150, 1250, 1350, and 1400 °C for 24 hrs. All three type of fibers showed no strength loss up to 1300°C. At 1400°C, the strength of the uncoated fibers dropped to about half the original value. Due to extreme brittleness and fragility, the PBN coated and Si-rich PBN coated fibers heat treated at 1400 °C could not be tested.

Exposure Effects on Fiber Surface and Microstructure

SEM analysis of the fiber surface indicated no perceptible change in the surface morphology of the uncoated fibers heat treated up to 1600 °C in nitrogen for 1 hr. Samples heat treated at 1800 °C showed nodules growing on the surface of the fiber (not shown). The PBN and Si-rich PBN coatings on the fibers remained intact after nitrogen heat treatment up to 1600 °C, but delaminated above this temperature. In contact with silicon powder, the uncoated, PBN coated and Si-rich PBN coated fibers heat treated in N_2 at 1150, 1250, and 1350 °C for 24 hrs showed no indication of a chemical reaction. At higher temperature, however, all three type of fibers reacted with silicon powder; the uncoated fiber reacted the most.

In order to evaluate time and temperature effects on the microstructure, the longitudinal sections of the fibers were observed under a TEM. The microstructure of the as-received uncoated fibers showed very fine (average diameter 11 ± 4nm) and randomly oriented SiC grains, which could be seen clearly in the dark field image, as shown in figure 6(a), throughout the cross section . After thermal exposure, coarsening of SiC grains surrounded by amorphous regions was observed in the microstructure. At temperatures to 1400°, SiC grain growth was slow with exposure time. For example, even after 400 hr exposure at 1400 °C, the average size of the SiC grains was ~ twice that of the as-received uncoated fibers. At temperatures >1500 °C, SiC grain growth was accelerated. After 1 hr heat treatment at 1800 °C, average grain diameter of SiC grains was ~3 to 4 times (~40 ± 15 nm) that of the untreated as-received fibers; but after 100 hr exposure at the same temperature, these grains grew to an average diameter of ~80 ± 30 nm (fig. 6(b)). Apart from the crystalline SiC phase, the fiber also contained significant amount of an amorphous phase, which was rich in carbon and bordered the SiC grains. This phase also coarsened with heat treatment time and temperature.

DISCUSSION

In general, polymer derived SiC fibers contain SiC microcrystals, excess carbon, and silicon oxycarbide. The amounts of excess phases present in the fiber vary depending on the pyrolysis conditions and curing methods used. Thermally induced degradation mechanisms of polymer derived SiC fibers are generally related to two accepted mechanisms: decomposition of silicon oxycarbide leading to increased porosity and flaw growth, and grain growth of the microcrystalline SiC that exists in the as-produced fiber (refs. 4 to 6). It has been shown previously that the thermal degradation occurring in the earlier grades of polymer derived SiC fibers was due to decomposition of silicon oxycarbide and could be delayed by heat treating them in high pressure argon (ref. 12), but the coarsening of the SiC grains could not be avoided.

The Hi-Nicalon fibers used in the current study contain microcrystalline SiC, excess carbon, and a small amount of silicon oxycarbide (ref. 7). Thermodynamically, the silicon oxycarbide phase should decompose, and SiC grains should grow above certain temperature depending on the exposure conditions. If the decomposition reaction is one of the dominant reactions responsible for thermal degradation of the fibers, then heat treating the fibers under high pressure nitrogen should delay the reaction. The high pressure nitrogen results showed no change in the onset of degradation temperature, and TEM results showed no evidence of internal porosity in the heat treated fibers. Both these results suggest that decomposition reaction may not be a dominant reaction responsible for the strength degradation. On the other hand, TEM results reveal increase in grain diameter with increasing heat treating temperature and time. Correspondingly, the strength of the fibers generally decreased with increasing grain diameter indicating that flaws associated with grain growth is the main factor responsible for strength degradation. The observed grain growth appears to be an intrinsic phenomena and is not influenced

by the surface coatings, or by the heat treating environment used in this study. The coarsening of SiC grains with heat treatment temperature and time is certainly related to lowering of the grain boundary surface energy, but the role of excess carbon and silicon oxycarbide in accelerating this growth is not clear. The fact that grain growth is observed at temperature as low as 1400 °C suggests that it may be promoted by impurities present in the as-received fibers, which certainly requires further study.

Results of this study also indicate that in contact with silicon powder, the uncoated, PBN coated, and Si-rich PBN coated fibers were stable only to 1350 °C. However, above this temperature, SEM studies showed that severe chemical reaction occurred between silicon powder and the fibers, possibly due to the formation of SiC on the surface of the fibers. Inability of the coatings to prevent such reactions probably related to porosity or imperfections present on the coating layers.

SUMMARY OF RESULTS AND CONCLUSIONS

The effects of temperature, time, and nitrogen pressure on strength and microstructural stability of uncoated, PBN coated, and Si-rich PBN coated fibers were determined. Strength stability of all three types of fibers under reaction-bonded silicon nitride processing conditions was evaluated. Key results are follows.

(1) In nitrogen environment, uncoated fibers showed significant strength degradation above 1400 °C. Surface coatings (PBN and Si-rich PBN), nitrogen over pressure, and exposure environments showed no significant influence on the onset of strength degradation. Microstructural characterization results indicated that the strength degradation is caused primarily by the flaws formed due to growth of SiC microcrystals.

(2) In contact with silicon powder and nitrogen, the uncoated and coated fibers degrade above 1350 °C. Formation of SiC as a result of chemical reaction between the excess carbon present in the fiber and silicon powder was the most likely mechanism for the strength degradation. Surface coating the fibers with a layer of CVD PBN or CVD Si-rich PBN did not prevent this reaction.

Thus it can be concluded that: (1) in inert environments, upper temperature capability of the uncoated Hi-Nicalon SiC fibers is limited to ~1400 °C; and (2) under RBSN processing conditions, Hi-Nicalon SiC fibers are stable only up to 1350 °C. Surface coatings may not be helpful in protecting the fibers from degradation.

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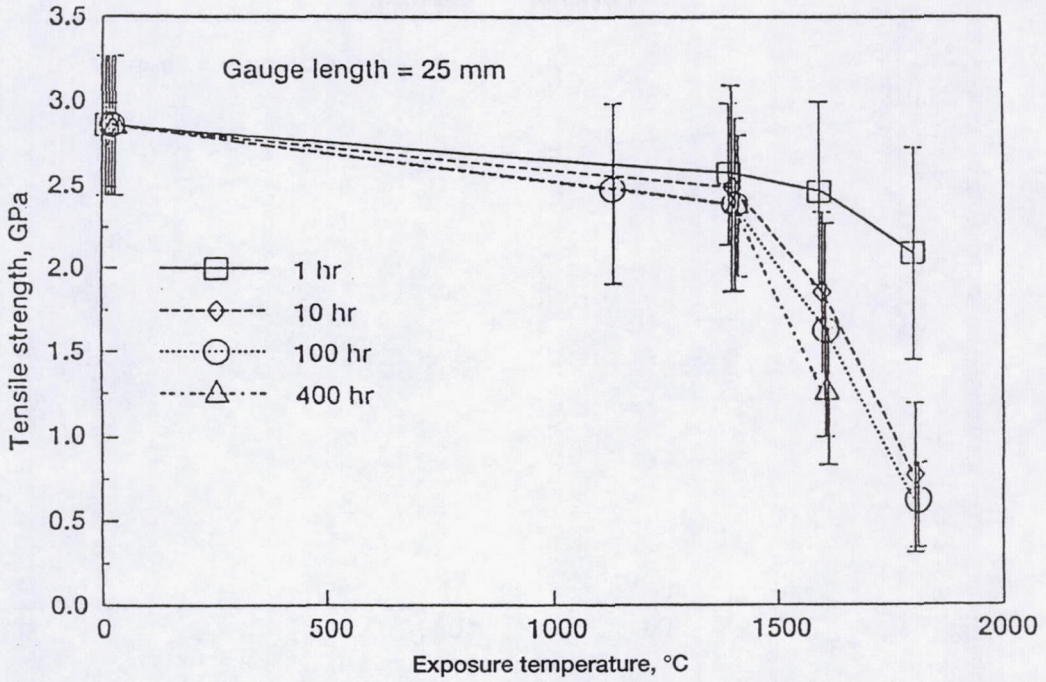

Figure 1.—Time and temperature effects on room temperature tensile strength of uncoated Hi-Nicalon SiC fibers heat treated in 0.1 MPa in nitrogen.

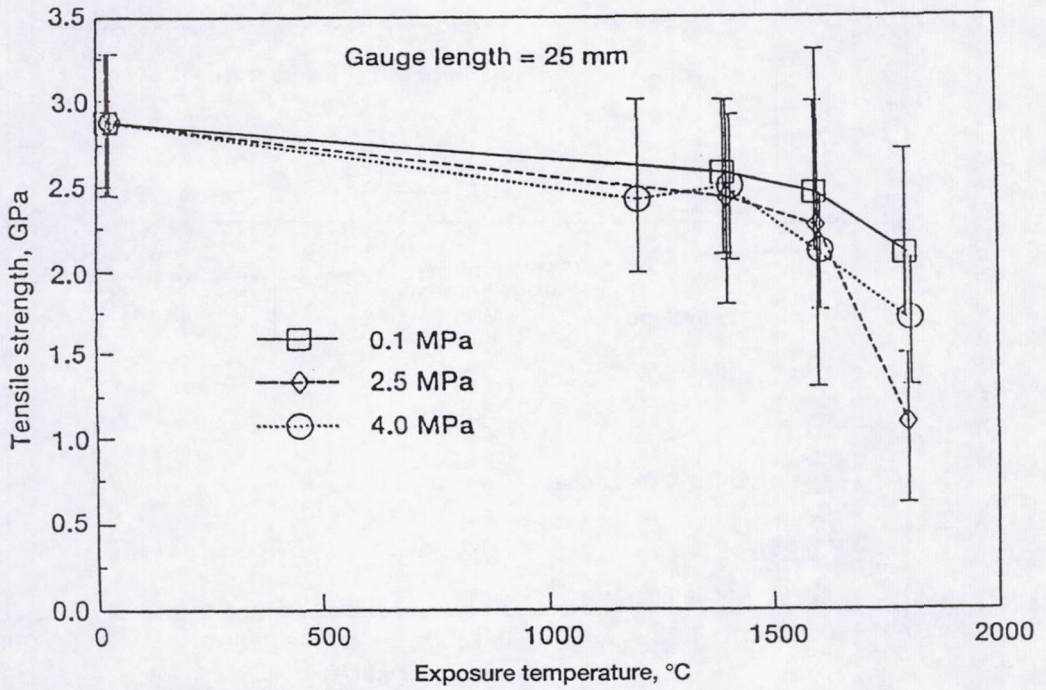

Figure 2.—Effects of pressure and temperature on room temperature tensile strength of uncoated Hi-Nicalon SiC fibers heat treated in 0.1 MPa nitrogen for 1 hr.

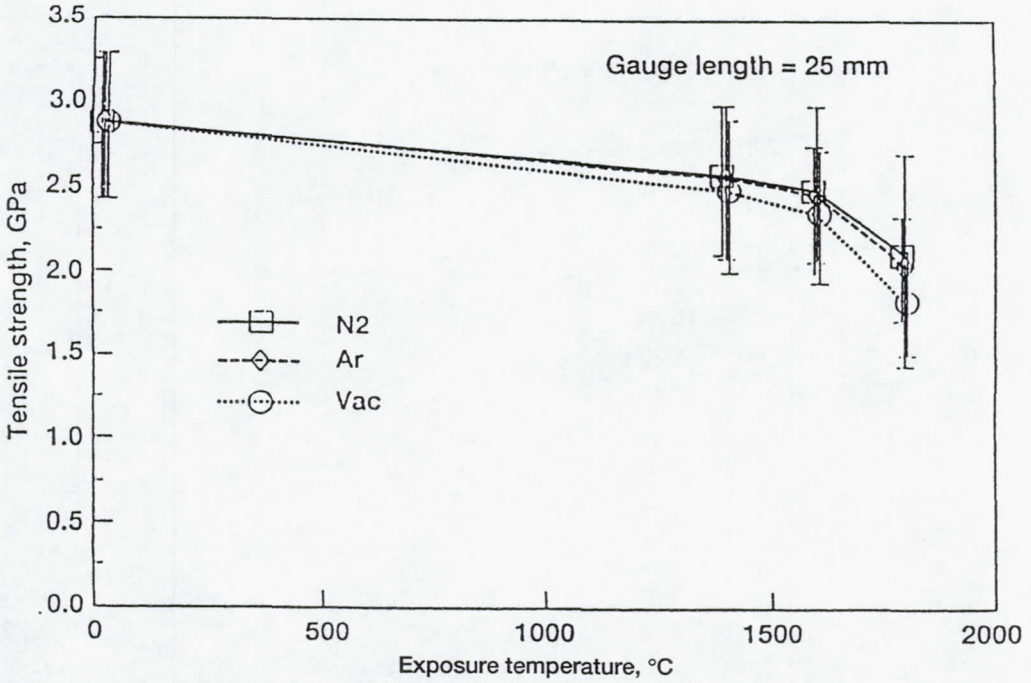

Figure 3.—Effects of environment and temperature on room temperature tensile strength of uncoated Hi-Nicalon SiC fibers heat treated for 1 hr.

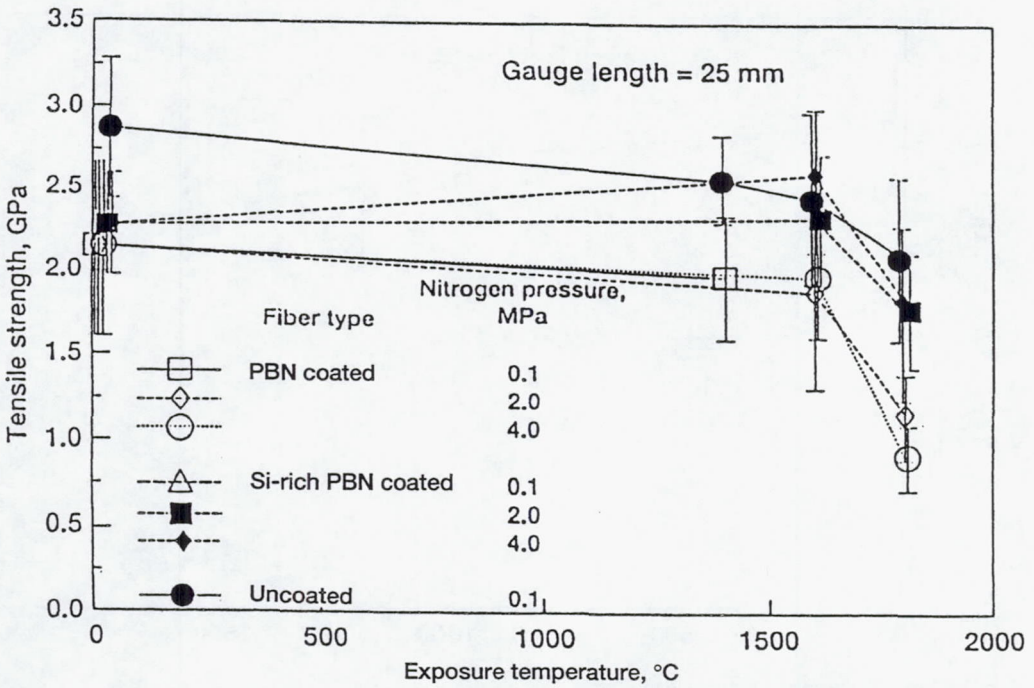

Figure 4.—Pressure and temperature effects on room temperature tensile strength of PBN and Si-rich PBN coated Hi-Nicalon SiC fibers heat treated for 1 hr in nitrogen.

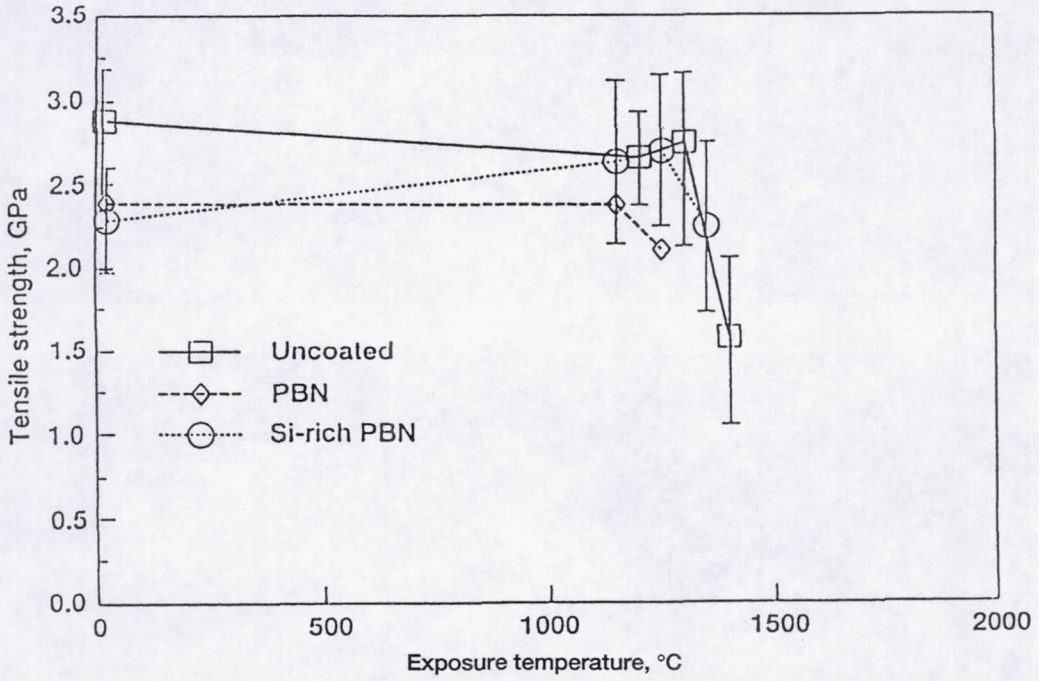

Figure 5.—Room temperature tensile strength of uncoated, PBN and Si-rich PBN coated Hi-Nicalon SiC fibers after 24 hr heat treatment in 0.1 MPa nitrogen and in contact with silicon powder.

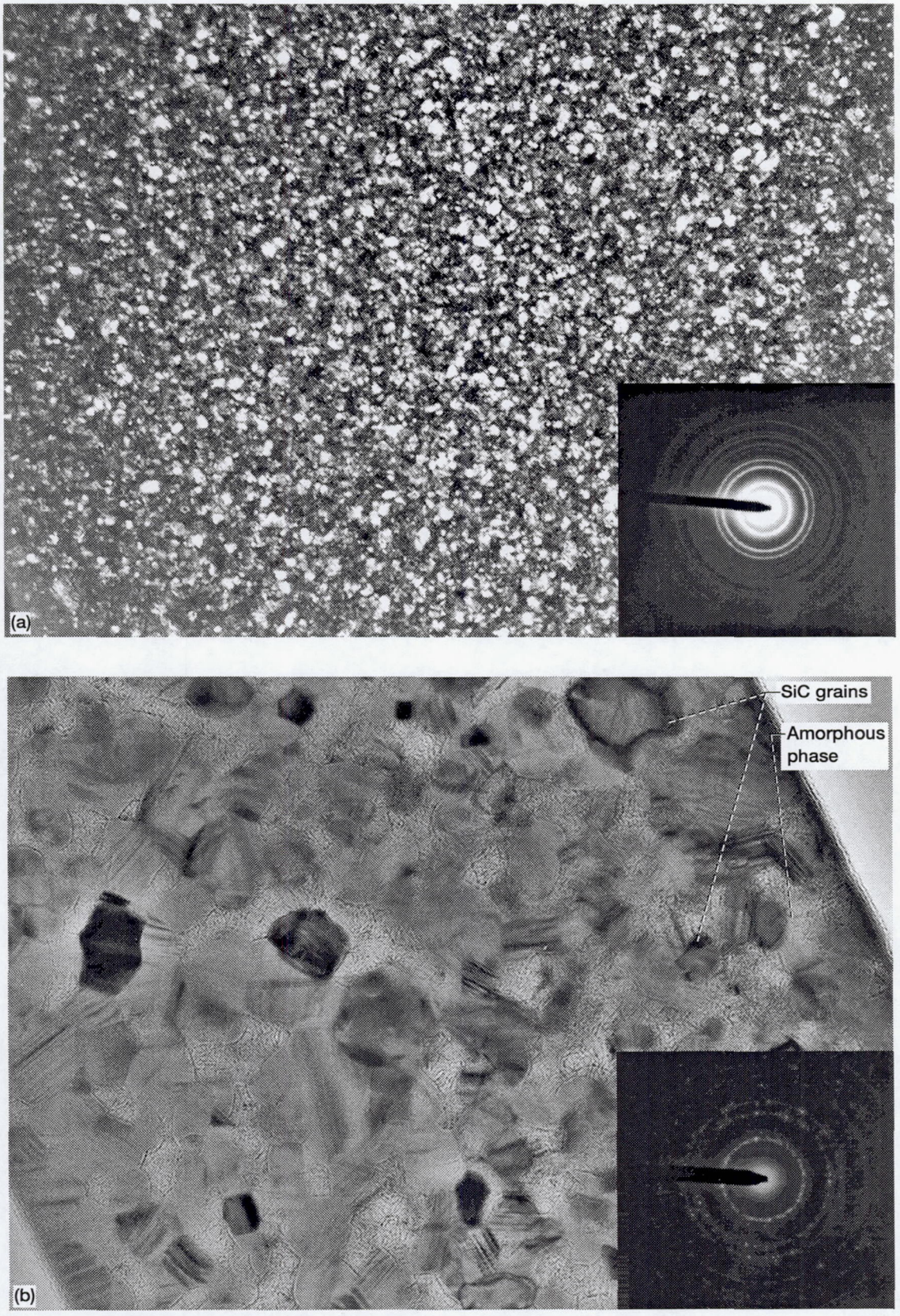

Figure 6.—TEM micrographs showing microstructure of the longitudinal sections of uncoated Hi-Nicalon SiC fibers. (a) As-received (dark field image). (b) After heat treatment in nitrogen at 1800 °C for 100 hr (bright field image).

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13. ABSTRACT ***(Maximum 200 words)***

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